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**Surface Crystallographic Dependence of Voltammetric  
Oxidation of Polyhydric Alcohols and Related Systems  
at Monocrystalline Gold-Acidic Aqueous Interfaces**

by

Antoinette Hamelin, Yeunghaw Ho, Si-Chung Chang,

Xiaoping Gao and Michael J. Weaver

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Langmuir

Purdue University

Department of Chemistry

West Lafayette, Indiana 47907

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## ABSTRACT

The voltammetric oxidation in aqueous 0.1 M  $\text{HClO}_4$  of four polyhydric alcohols, ethylene glycol, glycerol, meso-erythritol, and d-mannitol, on seven oriented gold surfaces, Au(111), (100), (110), (221), (533), (311), and (210), is reported with the objective of assessing the role of surface crystallographic orientation on the catalytic electrooxidation of such polyfunctional reactants. (The atomically well-ordered nature of these gold surfaces has been scrutinized by in-situ scanning tunneling microscopy.) In particular, the Au(221) and (533) faces were selected since they provide stepped surfaces, 4(111)-(111) and 4(111)-(100), respectively. The results are compared with corresponding data for simple unifunctional reactants, specifically for formic acid oxidation and with results reported previously (ref. 7) for carbon monoxide oxidation. In contrast to the last reaction, the electrooxidation rates for both the polyhydric alcohols and formic acid are greatest on Au(111), with Au(110) displaying unusually low activity. While formic acid electrooxidation is insensitive to the presence of mono-atomic surface steps, the polyhydric alcohols (especially mannitol) are substantially less reactive on Au(221) and (533) relative to Au(111). This behavioral difference is ascribed to stereochemical limitations on adsorption of the larger polyfunctional reactants imposed by the periodic surface steps. Such steps and other sites having low surface atomic coordination numbers are important for the alcohol oxidations, contrasting their strongly catalytic behavior for CO electrooxidation.

## INTRODUCTION

A fundamental issue in electrochemical kinetics concerns understanding the sensitivity of reaction rates at monocrystalline metal electrodes to the surface crystallographic orientation. This effect is of particular interest for inner-sphere processes, since the marked differences in electronic and stereochemical properties between various surface crystallographic orientations are anticipated to exert important influences upon the reaction rates via the state of the adsorbed intermediate(s). While investigations of this type are not yet abundant, such studies here become more feasible with the emergence of reliable procedures for preparing ordered single-crystal surfaces, especially for sp and sd metals (such as gold and silver)<sup>1</sup> and platinum.<sup>2</sup>

While gold is commonly considered to be a poor catalyst for gas-phase heterogeneous processes, its electrocatalytic properties are of substantial interest. This is due in part to the large potential ranges available for faradaic electrochemistry on gold even in aqueous media. In addition to the low-index surfaces, a number of stepped and other high-index gold faces have been studied in acidic aqueous media, primarily with respect to the voltammetry of anodic oxide formation and reduction and anion specific adsorption.<sup>1</sup> Electrochemical kinetic studies at various gold crystallographic orientations have been reported recently for several reactions: the reduction of cobalt amines<sup>3</sup> and protons,<sup>4</sup> and the oxidation of hydrogen,<sup>5</sup> carbon monoxide,<sup>6,7</sup> and formic acid<sup>8</sup> in acidic media, and the oxidation of ethylene glycol<sup>9</sup> and glucose<sup>10</sup> in alkaline solutions.

By and large, the observed kinetics in these studies display a marked and varied dependence on the gold crystallographic orientation. Notable in this regard is CO electrooxidation, for which the rates at a given electrode potential increase, for example, by ca 100 fold from Au(111) to Au(110).<sup>7</sup> At least for proton reduction<sup>4</sup> and CO oxidation,<sup>7</sup> the rate-crystal face depen-

dencies can be understood largely in terms of variations in the bonding energetics and stereochemical properties of specific surface sites. Such findings are not unexpected since such small reactants (and hence the ensuing adsorbed intermediates) probably bind only to 1-2 adjacent surface atoms.

Somewhat different behavior, however, would be anticipated for larger, especially polyfunctional, reactants that might bind over more extended distances on the metal electrode, and thereby be susceptible to dissimilar surface stereochemical factors. The examination of the electrooxidation kinetics of polyfunctional organic molecules should prove illuminating in this regard. Polycrystalline gold is known to be a good electrocatalyst for the oxidation of a variety of such species in alkaline media.<sup>11</sup> While often less effective in acidic media,<sup>11</sup> a number of polyfunctional species, especially polyhydric alcohols, commence electrooxidation at gold at potentials below those corresponding to surface oxidation (vide infra).

Given our recent interest in gold crystallographic effects upon the electrooxidation kinetics of small unifunctional species in acidic media,<sup>4,6,7</sup> we deemed it worthwhile to initiate a corresponding examination of some polyfunctional organic reactants under similar conditions. Some pertinent findings from this preliminary survey are reported here. These include the comparative voltammetric behavior of the polyhydric alcohols ethylene glycol, glycerol, meso-erythritol, and d-mannitol, which contain two, three, four, and six carbons/hydroxyl groups, respectively. Corresponding data are also reported for the electrooxidation of the uni- and difunctional reactants formic acid and oxalic acid. Linear sweep voltammetric data were gathered for these reactions on seven gold crystallographic orientations: Au(111), (100), (110), (221), (533), (311), and (210). The last surface was selected since it is "rough" on the atomic scale compared with the low-index faces, the gold surface atoms having a relatively low average coordina-

tion number. The Au(221) and (533) surfaces were chosen since they are formally stepped faces, denoted as<sup>12</sup> 4(111)-(111) and 4(111)-(100), respectively. [Note that 4(111)-(111) could also be denoted 3(111)-(110).]

One possible complication in interpreting electrocatalytic data on such monocrystalline gold electrodes is that reconstruction is known (or suspected) to occur at such surfaces not only in ultrahigh vacuum<sup>13</sup> but also in electrochemical environments.<sup>14-22</sup> Most recently, direct in-situ evidence for reconstruction at low-index gold-aqueous interfaces has been obtained by second harmonic generation,<sup>17</sup> grazing incidence x-ray diffraction,<sup>18</sup> and atomic-resolution scanning tunneling microscopy (STM).<sup>19-22</sup> The implications of these findings for the present study are noted below. However, in-situ STM data from our laboratory show that the surface reconstruction is largely lifted at the relatively positive potentials of interest here.<sup>19-22</sup> Moreover, recent STM results<sup>22</sup> (also see below) show that reconstruction on the present high-index faces is entirely absent under these conditions.

## EXPERIMENTAL

The preparation of the gold single-crystal faces was undertaken in LEI-CNRS, as outlined in the Appendix of ref. 23. The geometric area of most faces was either about 7 or 19 mm<sup>2</sup>. Each surface was cleaned immediately prior to use by heating in an oxy-gas flame, cooled in ultrapure water and transferred to the electrochemical cell, avoiding exposure to the laboratory atmosphere. Contact with the solution was made, the "raised meniscus" procedure being utilized so to yield a defined surface area ( $\pm 5\%$ ).<sup>1</sup>

The organic reactants were obtained from Aldrich. Perchloric acid (Merck Suprapur or G.F. Smith) and sulfuric acid (G.F. Smith) were employed as supporting electrolytes. The water was purified by a Millipore system. The electrochemical solutions were both purged and blanketed with purified nitrogen or argon. The counter electrode consisted of gold wire. All potentials

are quoted versus the saturated calomel electrode (SCE), and all measurements were performed at room temperature,  $23 \pm 1^\circ\text{C}$ .

## RESULTS

### Formic Acid and Oxalic Acid

Following electrode pretreatment, the surface was examined in the supporting electrolyte alone, usually  $0.1\text{ M HClO}_4$ , by using cyclic voltammetry so to characterize the interfacial state. The voltammetric sweep rate was  $50\text{ mV s}^{-1}$ , usually between  $-0.4\text{ V}$  and ca  $1.4\text{ V}$  vs SCE. Typical voltammograms so obtained for Au(100) and (110) are depicted as dotted traces in Figs. 1A and B, respectively. The current-potential profiles so obtained provide a useful check on the surface order and cleanliness.<sup>1</sup> The voltammograms are entirely reproducible upon repeated potential cycling. After satisfactory voltammograms were obtained in  $0.1\text{ M HClO}_4$  alone, the electrode was transferred to another electrochemical cell containing the desired reactant concentration. A drop of electrolyte protected the surface from contamination during the transfer.

Typical anodic-cathodic voltammograms ( $50\text{ mV s}^{-1}$ ) recorded for  $45\text{ mM}$  formic acid in  $0.1\text{ M HClO}_4$  on Au(100) and Au(110) are shown as solid traces in Figs. 1A and B, respectively. In both cases, formic acid electrooxidation as discerned from the anodic current commences at potentials,  $0$  to  $0.2\text{ V}$ , considerably below those, ca  $1.0\text{ V}$ , corresponding to the onset of anodic oxide formation. Substantial additional oxidation occurs within the region where anodic oxide formation occurs, as evidenced by the sharp voltammetric peak at ca  $1.2\text{ V}$  (Fig. 1). Provided that the potential-sweep direction is reversed prior to anodic oxide formation, the current-potential ( $i$ - $E$ ) curves obtained for positive- and negative-going sweeps are closely similar (see dashed traces in Figs. 1A and B). For potential sweeps continued into the anodic oxide region, the subsequent return sweep yielded comparable  $i$ - $E$  traces



once surface oxide reduction had been completed (see negative-going potential segment of solid traces, Fig. 1A, B). While most potential scans were initiated from -0.4 V, identical anodic voltammograms were obtained by selecting initial values from ca -0.4 to 0 V.

Altering the potential sweep rate over the range 20 to 500 mV s<sup>-1</sup> also yielded virtually no changes in the faradaic currents for formic acid oxidation, at least in the potential region prior to anodic oxide formation. This observation is not unexpected since the oxidation currents are insufficient to yield significant diffusion polarization. This circumstance also applies to the other reactions examined here. In this context, it should be recognized that the anodic voltammetric peaks observed for formic acid oxidation in Fig. 1, as well as for the reactions described below, are not due to the effects of reactant diffusion. Instead, the peaks probably arise from the passivating effects of surface oxidation, which is a well-known phenomenon in the electrocatalysis of organic molecules.

Comparable voltammetric behavior was obtained with the other four gold faces. Figure 2 displays representative anodic voltammograms obtained for 45 mM formic acid in 0.1 M HClO<sub>4</sub> at all six gold faces and also for polycrystalline gold under the same conditions as in Fig. 1. For clarity, the data for these seven surfaces are separated into two groups (Figs. 2A and B) with the Au(100) data being displayed in both figures so to aid the visual intercomparison. These results show that the kinetics of formic acid electrooxidation differ significantly between these various surfaces. Quantitative comparison of the observed behavior is hampered by the markedly different current-potential waveshapes that are observed. However, at least in the potential region prior to surface oxidation where substantial formic acid oxidation occurs, ca 0.6-0.7 V, the order of reactivity is (111) ≥ (221) - polycrystalline > 100 - (311) - (210) > (110). Similar voltammetric features

were obtained for 5 mM formic acid in 0.1 M HClO<sub>4</sub> on these surfaces, except that the anodic currents were ca 3 fold lower than for 45 mM reactant. Increasing the formic acid concentration over the range 50-200 mM yielded only relatively small ( $\leq 1.5$  fold) current increases, indicative of reaction orders substantially below unity.

An earlier study of formic acid oxidation on polycrystalline gold indicated that formic acid oxidation occurs only at the onset of gold surface oxidation.<sup>24</sup> This significant difference with the present results probably arises from the use of sulfuric, rather than perchloric, acid electrolyte in ref. 24 (vide infra).

A cursory examination was made of the voltammetric electrooxidation of oxalic acid under similar conditions. A representative set of anodic voltammograms obtained for 45 mM oxalic acid in 0.1 M HClO<sub>4</sub> on four gold faces is shown in Fig. 3. In contrast to formic acid, the electrooxidation of oxalic acid under these conditions is seen to be relatively insensitive to the gold crystallographic orientation. Thus the voltammetric peak currents and wave-shapes are almost identical on Au(111), (100), and (210), although the reaction commences at significantly (ca 80 mV) lower potentials on Au(100) (Fig. 3). Note, however, that the onset of oxalic acid oxidation, at ca 0.7 V, occurs on all gold faces at substantially more positive potentials than for formic acid oxidation. Comparable behavior was also obtained on polycrystalline gold, the voltammograms being intermediate between those observed on Au(110) and (210). While the peak currents for oxalic acid oxidation approach those expected for diffusion control, the voltammograms are virtually independent of stirring except at potentials positive of this peak region. The reproducibility of the current-potential curves during positive- and negative-going potential scans was similar to that observed for formic acid oxidation.

### Polyhydric Alcohols

The voltammetric behavior of methanol was also examined under similar conditions. However, no evidence for significant electrooxidation was found. Unlike this parent monohydric alcohol, however, substantial electrooxidation of vicinal polyhydric alcohols is observed on gold single crystals in acidic media. Of the four polyhydric alcohols examined here, the most clearcut behavior was observed for glycerol (trihydric,  $C_3$ ). Figure 4A displays typical anodic voltammograms for 0.1 M glycerol in 0.1 M  $HClO_4$  on Au(111), (221), and (110); Fig. 4B shows corresponding data on Au(533), (210), and (100). While the observed currents at potentials above ca 1.0 V contain contributions from surface oxide formation, especially for the less electrocatalytic faces, at least the voltammograms below this point arise largely from glycerol electrooxidation.

Interestingly, these voltammograms display a marked sensitivity to the gold crystallographic orientation. As for formic acid oxidation, the establishment of a quantitative reactivity sequence is hampered by the disparate waveshapes obtained on the different gold faces. This is emphasized, for example, by a comparison of Au(111) and (100): while the onset of significant current occurs at a lower potential on the latter surface, the former face displays much larger peak currents. Consequently, then, deducing even a qualitative reactivity sequence is contingent upon the electrode potential chosen. Nevertheless, at ca 0.8 to 0.9 V the sequence is: Au(111) > (221) ~ (533) > (100) ~ (210) > (110). We discuss this interesting reactivity trend below, after examining data for the other polyhydric alcohols.

A complicating feature, however, is observed for each of the polyhydric alcohols studied here. While the data in Fig. 4 are entirely reproducible if the voltammetric scans are initiated from -0.4 V, or at least negative of 0 V, holding the potential at values positive of ca 0.1 V before initiating

the sweep results in progressively smaller voltammetric currents. This "poisoning" effect was particularly prelevant on the Au(100) face, more than 10 fold diminutions in current often being obtained (vide infra). A similar phenomenon can also be discerned by altering the sweep rate, in that the voltammetric currents increase as the sweep rate increases, and hence as the oxidation timescale decreases. While this effect hinders quantitative interpretation of the voltammetric behavior, it nonetheless does not preclude a qualitative assessment of the surface crystallographic dependence.

Substantial differences in the anodic voltammetry of glycerol were also observed if 0.1 M  $\text{H}_2\text{SO}_4$  was substituted for 0.1 M  $\text{HClO}_4$ . In the former supporting electrolyte, glycerol electrooxidation is almost entirely inhibited at potentials below where surface oxide formation commences. This is the case even for Au(111) and (100), which display facile glycerol electrooxidation in 0.1 M  $\text{HClO}_4$ . A similar inhibition is seen for CO electrooxidation on gold in sulfuric acid electrolyte.<sup>7</sup>

The electrooxidation of d-mannitol (hexahydric,  $\text{C}_6$ ) on gold in 0.1 M  $\text{HClO}_4$  yielded a similar dependence on the crystallographic orientation as for glycerol, although the anodic currents are larger for the former reactant. Typical anodic voltammograms obtained at  $50 \text{ mV s}^{-1}$  from -0.4 V for 0.1 M mannitol in 0.1 M  $\text{HClO}_4$  are displayed in Figs. 5A and B, in the same format as for glycerol in Fig. 4. A similar dependence of the voltammetry for d-mannitol on the gold crystallographic orientation is observed as for glycerol, even though the greater electrocatalysis on Au(111) relative to Au(221) and (533) is especially marked for this reactant. An additional similarity is the diminution of the voltammetric currents for mannitol oxidation, especially on Au(100), caused by holding the potential at progressively more positive potentials prior to initiating the potential sweep. This effect is illustrated for mannitol electrooxidation on Au(100) in Fig. 6. Curves

1-3 were obtained sequentially by holding the potential for at least 20-30s at -0.4, 0, and 0.3 V before starting the  $50 \text{ mV s}^{-1}$  potential sweep. (The voltammogram obtained for  $0.1 \text{ M HClO}_4$  alone is shown as the dotted curve in Fig. 6). Curve 1 can be recovered entirely following this sequence by cycling the potential to 1.4 V and starting again from -0.4 V.

By comparison with glycerol and d-mannitol, the electrooxidation kinetics of ethylene glycol ( $\text{C}_2$ ) and meso-erythritol ( $\text{C}_4$ ) are sluggish on gold in  $0.1 \text{ M HClO}_4$ , only relatively small anodic currents being obtained prior to the initiation of gold surface electrooxidation. Typical anodic voltammograms are shown for  $0.1 \text{ M}$  ethylene glycol and erythritol in Figs. 7 and 8, respectively. Data for only two gold faces, Au(111) and (210) are shown in Figs. 7A, 8A, and 7B, 8B, respectively, for clarity since the currents are sufficiently small so to be comparable to those obtained in the absence of reactant. (The corresponding voltammograms obtained in  $0.1 \text{ M HClO}_4$  alone are shown as dotted traces in Figs. 7 and 8). The sluggish electrooxidation of these reactants hampers the data interpretation. Nevertheless, the morphology of the voltammograms and their dependence on the gold crystallographic orientation is qualitatively similar to that observed for glycerol and mannitol, although the extent of this dependence is somewhat smaller for ethylene glycol.

Beyond the electrooxidation currents themselves, the question arises of the reaction products that are formed under voltammetric conditions. We have shown that a useful tactic for this purpose involves recording sequences of real-time infrared spectra during slow voltammetric sweeps, utilizing a thin-layer spectroelectrochemical cell.<sup>25</sup> This "single-potential alteration infrared spectral" (SPAIRS) approach enables information to be obtained regarding the identity and formation kinetics of solution intermediates and products.<sup>23</sup> Some preliminary experiments of this type were performed here

for the electrooxidation of 0.1 M glycerol and mannitol in 0.1 M HClO<sub>4</sub> on Au(111). Both reactions yielded substantial CO<sub>2</sub> formation as discerned from the characteristic 2343 cm<sup>-1</sup> band,<sup>25</sup> but only at higher overpotentials and longer times where anodic oxide formation occurs. In addition, a band at 1740 cm<sup>-1</sup> was observed during the initial stages of glycerol, but not mannitol, electrooxidation. This feature, probably a carbonyl vibration, is consistent with the formation of aldehyde species; the lack of substantial carboxylic acid production (which would also yield a carbonyl stretch) was discerned from the observed absence of a C-O vibrational band at 1200-1300 cm<sup>-1</sup> under these conditions (cf ref. 24).

## DISCUSSION

As noted above, interpretation of some aspects of the present results may be affected by the occurrence of surface reconstruction. All three low-index gold faces are known to reconstruct in ultra-high vacuum (uhv) in the absence of adsorbates.<sup>13</sup> This was suggested to occur also in electrochemical environments originally by one of us on the basis of capacitance-potential data.<sup>1,14</sup> More recently, evidence for surface reconstruction at low-index gold-aqueous interfaces has been obtained from emersion experiments into uhv,<sup>15,16</sup> and more directly from in-situ second harmonic generation,<sup>17</sup> grazing-incidence x-ray diffraction,<sup>18</sup> and in our laboratory by atomic-resolution STM.<sup>19-22</sup> The last technique yields detailed atomic-level information on the surface structures brought about by reconstruction. For example, Au(111) undergoes a subtle yet marked ( $\sqrt{3} \times 22$ ) relaxation,<sup>21</sup> Au(110)<sup>20</sup> yields a mixture of (1 x 2) and (1 x 3) patterns, and Au(100) displays a series of structures having symmetries close to (5 x 27).<sup>19</sup> However, such reconstruction is observed to be lifted at positive surface charges, especially in the presence of specific adsorption.<sup>17,21</sup> This latter circumstance corresponds to the conditions encountered here, especially given that the

reactants undergo extensive adsorption, so that the predominant presence of unreconstructed Au(111) and (100) terraces is most likely, albeit with some possible relaxation of the top layer of gold atoms.

We have recently undertaken a detailed in-situ STM study of a number of high-index gold faces in 0.1 M  $\text{HClO}_4$ , including the (221), (311), and (533) surfaces considered here. The findings will be available elsewhere.<sup>22</sup> It is pertinent to note here that the stepped surfaces display uniformly well-ordered monoatomic steps, as anticipated from a simple termination of the bulk lattice. An example of a large-scale unfiltered (yet atomic-resolution) image for Au(533) at -0.1 V vs SCE in 0.1 M  $\text{HClO}_4$  is given in Fig. 9. (See figure captions and refs. 19-22 for experimental details.) The well-ordered nature of the monoatomic steps, with three atoms discerned within each intervening terrace, is clearly evident. While some relaxation of the step atoms is seen at more negative potentials for such step surfaces, especially (311), no reconstruction is evident at the positive electrode charges of interest here. This finding is consistent with the observed success of the simple "terrace-ledge-kink" (TLK) model in describing the dependence of the pzc upon the gold crystallographic orientation.<sup>1,26</sup> Overall, then, it appears valid to discuss the crystallographic orientation effects observed here in terms of such a surface stereochemical picture.

It is instructive to compare and contrast the nature of the striking crystallographic-orientation dependence of the different oxidation processes examined here with that for carbon monoxide oxidation on gold reported elsewhere.<sup>7</sup> Comparison between this behavior for the polyhydric alcohols, formic acid, and carbon monoxide reveals notable differences. For the last reactant, the order of reactivities in 0.1 M  $\text{HClO}_4$  is<sup>7</sup>  $\text{Au}(110) > (210) > (221) \sim (100) \geq (533) > (111)$ . This reactivity sequence suggests that CO electrooxidation is favored at gold atomic sites having a lower coordination

number (and therefore a greater number of "dangling bonds"). Such sites, particularly prevalent on Au(110) and (210), have been shown by infrared spectroscopy to be energetically favorable for binding CO. This factor, along with the need for coadsorption of the water or hydroxyl oxidant in adjacent sites, is responsible, for example, for the markedly (ca 100 fold) higher CO electrooxidation rates on Au(110) with respect to (111).<sup>7</sup>

Significantly, the surface crystallographic dependence observed here for the electrooxidation of both formic acid and polyhydric alcohols are entirely different. Thus in complete contrast to CO electrooxidation, Au(111) provides the most, and Au(110) the least, catalytic surface for both these reaction types. Another notable difference concerns the behavior of the stepped faces Au(221) and (533) in relation to the low-index surface Au(111). For CO electrooxidation, the former two surfaces provide markedly (>10 fold) higher rates than Au(111), demonstrating the favorable nature of monoatomic step sites for this process. For formic acid, Au(221) yields closely similar voltammetric behavior as Au(111), indicating that the monoatomic steps exert little influence on the electrooxidation kinetics. Presumably, then, this process occurs preferentially on the (111) terraces.

For the polyhydric alcohols, especially for d-mannitol, however, the Au(221) and (533) faces yield markedly less facile electrooxidation compared with Au(111). This difference can be rationalized at least in part from the polyfunctional nature of these reactants. Thus it is likely that the polyol reactants adsorb on the metal via two or more hydroxyl groups. Given that the average width of the terraces on Au(221) and (533) is about 9Å, one can imagine that the binding of at least the larger polyfunctional reactants, and hence the electrooxidation rates, could be hindered substantially compared to adsorption on the extended terrace domains that are present on Au(111). The relatively minor hindrance to formic acid electrooxidation



seen upon substituting Au(111) by Au(221) is not unexpected on this basis given the small size of this reactant. The especially sluggish electrooxidation rates on Au(110) for both the polyols and formic acid can also be rationalized in this vein since this surface may be envisaged as the step face 2(111)-(111). The coordination geometry of even a small molecule such as formic acid will inevitably be quite different on Au(111) and (110).

Although the greatest electrooxidation currents for alcohol oxidation are obtained on Au(111), the other low-index face Au(100) also yields facile electrocatalysis in that the onset of electrooxidation generally occurs at significantly lower potentials than on the other surfaces. This behavior may arise in part from the substantially (ca 0.15 V) less positive potential of zero charge (pzc) for Au(100) compared with Au(111) in acidic perchlorate media (ca 0.09 and 0.24 V, respectively<sup>4</sup>). This factor together with the higher capacitances discerned voltammetrically<sup>27</sup> at potentials positive of the pzc yields significantly larger positive charges on Au(100) compared with Au(111), which may aid surface binding of the reactant hydroxyl group and hence accelerate the electrooxidation. The smaller oxidation currents observed at higher overpotentials on Au(100) versus Au(111) may be connected with the occurrence of "preoxidation" on Au(100),<sup>27</sup> as discerned readily from the enhanced currents seen beyond ca 0.6 V in 0.1 M HClO<sub>4</sub> alone. The adsorbed hydroxyl species and perchlorate formed under these conditions may act as an inhibitor for alcohol electrooxidation by diminishing the extent of reactant adsorption. The very marked inhibition of glycerol electrooxidation seen by substituting 0.1 M H<sub>2</sub>SO<sub>4</sub> for 0.1 M HClO<sub>4</sub> electrolyte probably arises from the bisulfate/sulfate adsorption that occurs in the former medium<sup>28</sup> (cf ref. 7).

Note that the oxidation of the alcohol to an aldehyde merely requires electron/proton transfer, rather than additional oxygen transfer (such as

from adsorbed hydroxyl) as in the case of carboxylic acid or  $\text{CO}_2$  formation. Consistent with this line of reasoning, the present SPAIRS results indicate that further oxidation of the alcohols beyond aldehydes to  $\text{CO}_2$  requires the occurrence of some gold surface oxidation. The differences in electrocatalytic behavior of Au(100) versus (111) for formic acid oxidation can be accounted for in the same manner as for the polyhydric alcohols, given that the formation of  $\text{CO}_2$  from formic acid also involves only a two electron/proton transfer, no oxygen addition being required. Further speculation on the mechanistic aspects of the present findings, however, appear unwarranted in the absence of conclusive evidence regarding the nature of the adsorbed reaction intermediates.

Regardless of such mechanistic details, the present findings attest to the rich diversity of surface crystallographic effects upon electrocatalytic oxidations on gold, depending on the reactant structure. The magnitude as well as variety of such effects is sufficiently large to justify more detailed examination. In order to attain a fuller understanding of the surface chemical factors that are involved, it would be desirable to obtain vibrational spectroscopic information on the structure of adsorbed intermediates, especially in conjunction with more extensive electrochemical rate measurements. We hope to report such measurements for a variety of organic reactions along with parallel atomic-resolution STM data on gold in the future.

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# FIGURE CAPTIONS

## Fig. 1

Anodic-cathodic cyclic voltammograms from -0.3 V at  $50 \text{ mV s}^{-1}$  for Au(100) (1A) and Au(110) (1B) in  $0.1 \text{ M HClO}_4$  alone (dotted curves) and containing  $0.045 \text{ M}$  formic acid (solid curves).

## Fig. 2

Positive-going voltammograms from -0.3 V at  $50 \text{ mV s}^{-1}$  for various gold faces, as indicated, in  $0.045 \text{ M}$  formic acid +  $0.1 \text{ M HClO}_4$  (poly - polycrystalline surface).

## Fig. 3

Positive-going voltammograms from -0.3 V at  $50 \text{ mV s}^{-1}$  for various gold faces, as indicated, in  $0.045 \text{ M}$  oxalic acid +  $0.1 \text{ M HClO}_4$ .

## Fig. 4

Positive-going voltammograms from -0.4 V at  $50 \text{ mV s}^{-1}$  for various gold faces, as indicated, in  $0.1 \text{ M}$  glycerol +  $0.1 \text{ M HClO}_4$ .

## Fig. 5

Positive-going voltammograms from -0.4 V at  $50 \text{ mV s}^{-1}$  for various gold faces, as indicated, in  $0.1 \text{ M}$  d-mannitol +  $0.1 \text{ M HClO}_4$ .

## Fig. 6

Anodic-cathodic cyclic voltammograms at  $50 \text{ mV s}^{-1}$  for Au(100) in  $0.1 \text{ M HClO}_4$  alone (dotted curve) and containing  $0.1 \text{ M}$  d-mannitol (curves 1-3) for different sequential initial potentials as follows: 1, -0.4 V; 2, 0 V; 3, 0.3 V. Potential held at initial value for ca 30s before each sweep. A repeat of voltammogram under the conditions of curve 1 recorded after curve 3 yielded identical trace to that of the former.

## Fig. 7

Anodic voltammograms from -0.4 V at  $50 \text{ mV s}^{-1}$  for Au(111) (A) and Au(210) (B) in  $0.1 \text{ M HClO}_4$  alone (dotted curves) and containing  $0.1 \text{ M}$  ethylene glycol (solid curves).

## Fig. 8

Anodic voltammograms at  $50 \text{ mV s}^{-1}$  for Au(111) (A) and Au(210) (B) in  $0.1 \text{ M HClO}_4$  alone (dotted curves) and containing  $0.1 \text{ M}$  meso-erythritol (solid, dashed curves). The initial potentials for the solid and dashed traces are -0.4 V and 0.3 V, respectively.

## Fig. 9

Unfiltered height-shaded STM image ( $30^\circ$  from surface normal) of Au(533) at -0.1 V vs SCE in  $0.1 \text{ M HClO}_4$ . Image was obtained in constant current mode (i.e., "height mode") with tip-surface bias voltage = 20 mV, tunneling current = 15 nA (see refs. 19-22 for procedural details).